ELSEVIER

Thermochimica Acta 264 (1995) 59–66

thermochimica acta

Thermal analysis of the crystallization of SAPO-5

Chr. Minchev [a,*], V. Valtchev [b], S. Mintova [b]

[a] *Institute of Organic Chemistry, Bulgarian Academy of Sciences, G. Bonchev St., 1040 Sofia, Bulgaria*
[b] *Central Laboratory of Minerology and Crystallography, Bulgarian Academy of Sciences, 92 Rakovski St., 1000 Sofia, Bulgaria*

Received 14 March 1995; accepted 29 March 1995

Abstract

The crystallization of microporous silicoaluminophosphate structure type 5 (SAPO-5) is studied by thermal analysis. The results obtained are compared with X-ray powder diffraction and IR spectroscopy data. The thermal effects determining the structure directing agents in the initial gel, in the intermediate X-ray powder diffraction amorphous product and in the final crystalline material are investigated.

Keywords: Kinetics; SAPO-5 crystallization; Thermal analysis

1. Introduction

Silicoaluminophosophate molecular sieves have (SAPO) been promoted as new materials with interesting physico-chemical and catalytic properties [1–4]. These materials are usually produced by hydrothermal crystallization of silicoaluminophosphate gels in the presence of appropriate organic agents (templates) [1] removed from the crystalline structure through heating in inert or oxidizing atmospheres at relatively high temperatures (400–600°C). Thus, combined TG- DTG-DTA methods can be successfully used to obtain information on the conditions of dissociation of various organic templates in silicoaluminophosphate and aluminophosphate molecular sieves [4–8]. At the same time, there is no data on the usage of thermochemical methods of analysis to study SAPO molecular sieves crystallization. These methods have been widely employed nowadays in characterizing other microporous materials like, for

* Corresponding author.

0040-6031/95/$09.50 © 1995 – Elsevier Science B.V. All rights reserved
SSDI 0040-6031(95)02410-7

example, molecular sieves with MFI type structure (IUPAC nomenclature) [9–11]. In this context, it becomes of interest to investigate the stages of crystallization of SAPO materials by means of thermal analysis. For this purpose samples of SAPO-5 with different degree of crystallinity were characterized using TG- DTG-DTA analysis, XRD and IR absorption spectroscopy.

2. Experimental

The SAPO-5 samples and the corresponding intermediate phases were prepared by heating at 160°C, 180°C and 200°C a mixture of reagents of the following molar composition:

$$R: 0, 2SiO_2 : Al_2O_3 : P_2O_5 : 50H_2O$$

where R is the organic template triethylamine (Et_3N).

With the exception of pseudoboemite (Condea) all raw materials, i.e. SiO_2 (extra pure), 85% H_3PO_4 (suprapure) and Et_3N (for synthesis) were obtained from Merck. The crystallization was conducted in separate teflon bottles placed in stainless steel autoclaves. The synthesis were interrupted after different time of heating and the samples so formed were washed, dried and rehydrated in a desiccator over saturated $Ca(NO_3)_2$ solution with 55% R.H..

The combined TG-DTG-DTA thermal analysis was conducted in a MOM OD-103 apparatus or in Sataram TG-DTG 92 under dry air flow, at a rate of 10 deg.min^{-1} as described in Ref. 7. The IR spectra (1400–300 cm^{-1}) were recorded with a Specord M80 spectrophotometer in KBr pallets. The X-ray spectra of the samples were measured by a DRON – 3B diffractometer with filtered Cu Kα radiation. The degree of crystallinity of the specimen (SAPO-5) was evaluated by comparing the area of selected peaks (18–24° 2θ) with the solid product and the reference sample. The scanning electron micrographs were taken with a SEM-Philips 515 apparatus. The elemental analysis for determining the carbon content was conducted as reported in Ref. 12.

3. Results and discussion

The results obtained for the series of samples synthesized at 160°C are given in Table 1 and Fig. 1. According to XRD data the samples can be classified in the following three groups:

(i) In the samples Nos. 1 and 2, X-ray data indicated an amorphous form, only traces of SAPO-5 are present in No. 2.

(ii) The intensity of the peaks corresponding to SAPO-5 in the XRD patterns of the samples Nos. 3–5 increases, while that of the amorphous halo decreases on rising the degree of crystallinity of the material.

(iii) The samples Nos. 6–8 show a high degree of crystallinity. In the DTG curves of the samples Nos. 1–5 (Fig. 1) one can see the characteristic features corresponding to

Table 1
TG and XRD data of samples obtained at 160°C

No.[a]	t/h[b]	T_g data, weight loss(%), stages					Temperature of DTG peaks/°C					XRD crystallinity (%)
		I	II	III	II+III	Total						
1	2	16.2	–	–	9.0	26.0	120	332	–	455	–	0
2	4	15.0	–	–	9.0	24.3	122	324	–	459	–	5
3	6	11.9	–	–	9.2	21.5	110	324	412	454	–	19
4	8	10.1	–	–	8.6	18.7	105	337	407	460	–	33
5	12	8.1	7.0	2.0	9.0	17.1	77	–	400	455	596	61
6	15	7.1	5.1	2.2	7.3	14.4	91	–	395	–	580	~85
7	17	7.2	5.1	2.4	7.5	14.7	95	–	397	–	582	~85
8	19	6.7	5.0	2.3	7.3	14.0	95	–	397	–	585	~85

[a] Sample number.
[b] Time of crystallization.

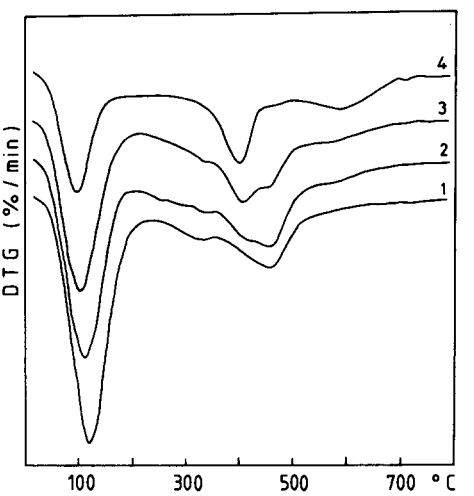

Fig. 1. DTG curves of the SAPO-5 crystallized for 2h(1), 4h(2), 6h(3), 12h(4) and 19h(5) at 160°C.

the processes of water evaporation and of the dissociation of the organic template. The samples whose crystallization was terminated during the first stages of growth ($t = 2$–6 h) are characterized by three main DTG peaks in the thermal curves, at about 120°C, 330°C and 455°C. The position and the intensity of the peaks indicated in Fig. 1 gradually change with increasing the time of crystallization, the maxima in the DTG curve of the final crystalline product being shifted to 95°C, 400°C and 580°C. The comparison between the data obtained by DTG and DTA (Fig. 2) and chemical analysis for the content of carbon reveals that these three effects correspond to the

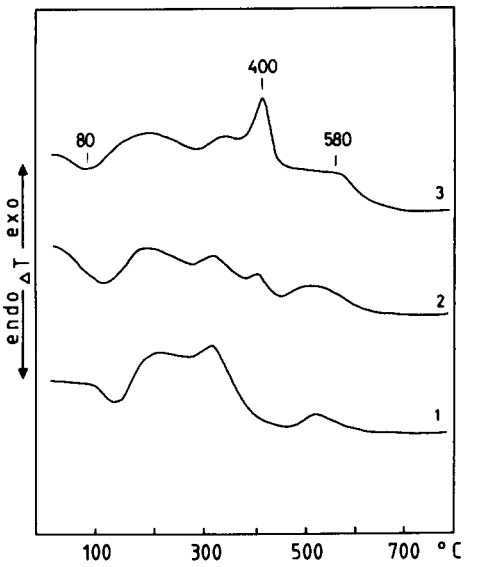

Fig. 2. DTA curves of the SAPO-5 synthesized for 2h(1), 8h(2) and 19h(3) at 160°C.

following temperature ranges: (i) dehydration (25–270°C), (ii) thermal oxidation destruction of the organic template (270–500°C) and (iii) extraction and complete burning of the products resulting from the dissociation of the template of SAPO-5 (500–700°C). One should say at that place that the peaks of the thermal effects in the DTA curves correspond to the maxima in DTG curves. The results obtained are in a good accordance with our earlier results on the thermal behavior of as-made SAPO-5, which speaks strongly in favour of a removal of organic material from the crystalline SAPO-5 [7].

The high content of amorphous phase in the samples 1–4 makes it difficult to interpret the thermal effects contributing to DTG curves. The existence of Et_3N in the amorphous samples as well as in those of low degree of crystallinity was detected through the carbon content. The content of carbon in samples 1–4 rises from 2.94% to 5.89%, although the general weight losses decrease (Table 1). The comparison of the data obtained by various methods shows that the removal of water takes place in the temperature range (20–230°C), whereas the organic amine escapes at 230–500°C. The total removal of Et_3N finishes at about 500°C. The effect appearing at 580°C in samples with high degrees of crystallinity is not observed in the DTG curves for samples Nos. 1–4. Consequently, the completely built microporous crystalline structure complicates the diffusion during the removal of the template and the products of its dissociation.

The content of water in the samples decreases gradually with increasing the degree of crystallinity in the range 16–7 wt% (Table 1). This result is not surprising when one keeps in mind that the amorphous phases of the intermediate samples are of a higher hydrophility than the crystalline one. The reduction of the intensity of the peaks at

330°C and 455°C is accompanied by the appearance and the intensifying of new effect at 400°C and 580°C (Fig. 1). The characteristic changes in DTA and DTG curves are obviously connected with serious variations and rearrangements in the reaction mixture. X-ray diffraction and IR absorption spectroscopy data reveal that the observed increase in the degree of crystallinity and are in good accordance with the thermal effect occurring at 400°C. It is interesting to mention the relatively high thermal stability of the template in X-ray amorphous samples and in those low degree of crystallinity. Similarly, as in the case of zeolite ZSM-5 [13], one can expect the formation of a stable complex of amine with the silicoaluminophosphate gel. Comparative studies revealed that the removal of Et_3N out of the gel not treated hydrothermally occurs at 200–260°C, i.e. at a considerably lower temperature. So, a stable X-ray amorphous complex of silicoaluminophosphate gel with organic amine forms during the hydrothermal crystallization, which transforms later in SAPO-5.

The results on samples synthesized at 180°C (Table 2, Fig. 3) and 200°C (Table 3) complete the aforesaid data for the series of samples produced at 160°C. At higher temperatures of crystallization the samples can be classified as follows:

(i) X-ray amorphous samples or materials with a low degree of crystallinity – samples 1 and 2, synthesized at 180°C and sample 1 synthesized at 200°C;

(ii) intermediate products - 3 and 4, synthesized at 180°C, and sample 2 synthesized at 200°C;

(iii) high-crystalline products – samples 5–7, synthesized at 180°C, and samples 3–6, synthesized at 200°C;

There are differences in the behaviour of TG curves for the samples of high degree of crystallinity synthesized at the three temperatures. In the samples formed at lower temperatures the content of water is higher, the amount of water decreasing down to 7.1% at 160°C, to 5.7–5.9% at 180°C and to 4.9–5.0% at 200°C. The samples differs as well in their degree of crystallinity evaluated according to the powder X-ray diffraction

Table 2
TG and XRD data of samples obtained at 180°C

No.[a]	t/h[b]	T_g data, weight loss(%), stages					Temperature of DTG peaks/°C					XRD crystallinity (%)
		I	II	III	II+III	Total						
1	2	15.2	–	–	10.0	25.2	119	317	–	453	–	6
2	4	9.3	–	–	10.6	19.9	110	341	408	454	–	35
3	6	8.0	–	–	8.9	16.9	101	332	406	458	–	51
4	8	5.2	5.5	2.0	7.5	12.7	95	–	403	462	597	76
5	12	5.8	5.3	2.3	7.6	13.4	90	–	401	–	599	~96
6	17	5.9	5.0	2.3	7.3	13.2	95	–	399	–	587	~95
7	19	5.7	4.9	2.4	7.3	13.0	93	–	398	–	585	~95

[a] Sample number.
[b] Time of crystallization.

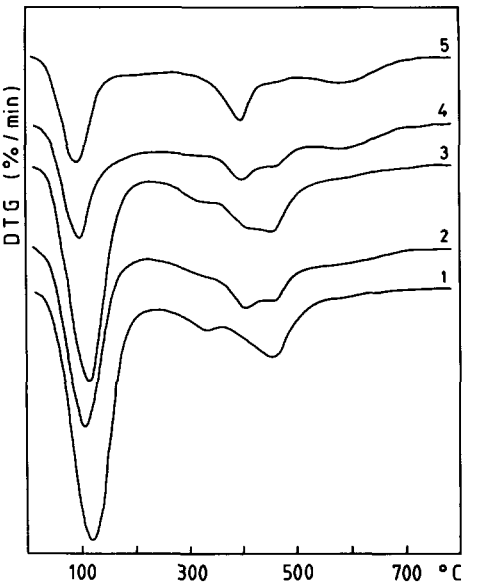

Fig. 3. DTG curves of SAPO-5 crystallized for 2h(1), 4h(2) 8h(3) and 19h(4) at 180°C.

Table 3
TG and XRD data of samples obtained at 200°C

No.[a]	t/h[b]	T_g data, weight loss(%), stages					Temperature of DTG peaks/°C					XRD crystallinity (%)
		I	II	III	II+III	Total						
1	2	11.9	–	–	10.0	21.9	108	344	–	430	–	29
2	4	5.7	–	–	8.1	13.8	91	–	401	447	588	76
3	6	5.7	4.3	3.0	7.3	13.0	82	–	399	–	603	100
4	8	5.1	5.0	2.5	7.5	12.6	89	–	402	–	604	100
5	12	4.9	5.5	2.2	7.7	12.6	88	–	400	–	600	100
6	22	4.5	5.5	2.3	7.8	12.3	82	–	405	–	605	100

[a] Sample number.
[b] Time of crystallization.

data (Tables 1–3). No other crystalline phases were detected, which indicates the amorphous structure of the remainder. Using SEM analysis non-crystalline-like product was observed in the sample synthesized at 160°C. The presence of non-crystallized silicoaluminophosphate gel explains the higher content of water in samples synthesized at 160°C and 180°C.

The degree of crystallinity was measured also by IR absorption spectroscopy. Fig. 4 presents IR spectra of the samples crystallized for 2,4,6 and 8 hours at 180°C. In the amorphous sample the absorption band at 366 cm^{-1}, is distinguished early and its intensity decreases with increasing the degree of crystallinity and vanishes in the

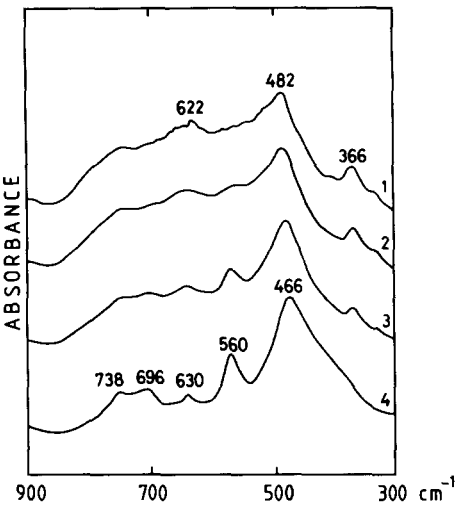

Fig. 4. IR spectra of the SAPO-5 crystallized for 2h(1), 4h(2), 6h(3) and 8h(4) 180°C.

fully-crystalline sample. Exactly opposite is the behaviour of the IR band at 560 cm^{-1}, the intensity of which rises on increasing the degree of crystallinity. The dependence of the spectral intensity of these two bands on the degree of crystallinity agrees well with that observed for the changes in the DTG curves of the samples.

4. Conclusion

The process of crystallization of SAPO-5 sieves is studied by thermal analysis. The results obtained correlate well with X-ray diffraction and IR absorption data on this material. It is shown that thermal analysis provides valuable information on the changes arising in the reaction mixture during the synthesis and on the process of micropore formation. The alteration in the temperature and the intensity of the thermal effects makes it possible to specify the organic species in the initial gel, in the intermediate X-ray amorphous product and in the final SAPO-5. The temperature maxima of these effects are in the ranges 200–260°C, 330–455°c and 400–580°C.

Acknowledgement

The financial support of this work by the Bulgarian Ministry of Science and Education under contract number X344-1993 is gratefully acknowledged. The authors thank Mr. V. Minkov for IR measurements and Dr. L. Konstantinov for valuable assistance.

References

[1] B.M. Lok, C.A. Messina, R.T. Gajek, T.R. Cannan and E. M. Flaningen, J. Am. Chem. Soc., 106 (1984) 6092.
[2] J.A. Rabo, R.J. Pellet, P.K. Conghlin and E.S. Shamshoum, Stud. Surf. Sci. Catal., 46 (1989) 1.
[3] J.A. Martens, P.J. Grobe P.A. Jacobs, and J. Catal., 126 (1994) 492.
[4] R. Borade, A. Clearfield, J. Mol. Catal, 88 (1994) 492.
[5] V.R. Choudhary and S.D. Sansare, J. Thermal. Anal., 32 (1987) 777
[6] N.J. Tapp, N.B. Milestone and D.M. Bibby, Stud. Surf. Sci. Catal., 37 (1988) 393.
[7] Ch. Minchev, H. Weyda, V. Minkov, V. Penchev and H. Lechert, J. Thermal. Anal., 37 (1991) 573.
[8] Ch. Minchev, V. Minkov, V. Penchev, H. Weyda and H. Lechert, J. Thermal. Anal., 37 (1991) 171.
[9] Z. Gabelica, J. Nagy, E. Derouane and J.P. Gilson, Clay Minerals, 19 (1984) 803.
[10] Z. Gabelica, J. Nagy, P. Bodart and A. Nastro, Therm. Acta, 93 (1985) 749.
[11] A. Nastro, J. Nagy, F. Crea, J. Lee, D. Hayhurst and G. Giordano, Therm. Acta, 133 (1988) 403.
[12] B. Stojanova-Ivanova, Kratak kurs po organichen analiz, Nayka i izkustvo, Sofia, 1967.
[13] F. Testa, F. Crea, A. Nastro, R. Aiello and J.B. Nagy, Zeolites, 11 (1991) 705.